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Mössbauer Spectroscopic Study on the Mixed-Valence States of 1′,1‴-Bis(*o*-methylbenzyl)-, 1′,1‴-Bis(*m*-methylbenzyl)-, and 1′,1‴-Bis(*p*-methylbenzyl)biferrocenium Triiodide

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Synopsis. 1′,1‴-Bis(*o*-methylbenzyl)-, 1′,1‴-bis(*m*-methylbenzyl)-, and 1′,1‴-bis(*p*-methylbenzyl)biferrocene were synthesized and Mössbauer spectroscopic measurements of their monocation salts were carried out at various temperatures in order to study the effect of the substituents on the mixed-valence states.

Biferrocene derivatives are easily monooxidized to give the corresponding monocations, which show a mixed-valence state. It is known that those compounds can be classified into two types of valence states of iron atoms, a trapped-valence type and an averaged-valence type, by means of Mössbauer spectroscopy.[1] The former type has different states of iron atoms corresponding to ferrocene-like bivalent and ferricenium-like tervalent iron atoms, while the latter has an equivalent state averaged over ferrocene-like bivalent and ferricenium-like tervalent iron atoms.

It has been reported that the triiodide salt of biferrocene itself is of the trapped-valence type from a low temperature to room temperature.[2] However, Iijima et al. observed the interesting temperature-dependence of the mixed-valence states for 1′,1‴-diethyl- and 1′,1‴-dipropylbiferrocenium triiodide which show an averaged-valence type near room temperature but a trapped-valence type at low temperatures.[3]

Recently, it was reported that the triiodide salts of monocationic 1′,1‴-di-*n*-butyl- and 1′,1‴-dibenzylbiferrocenium show a temperature-dependence similar to those observed in 1′,1‴-diethyl- and 1′,1‴-dipropylbiferrocenium triiodide, suggesting that the environment surrounding each cation in the solids should determine whether or not an intramolecular electron transfer occurs.[4]

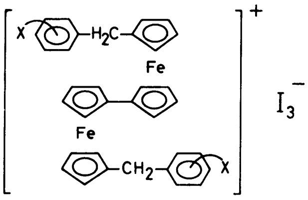

Fig. 1. Compounds.
(1) 1′,1‴-Bis(*o*-methylbenzyl)biferrocenium triiodide ($X{=}o\text{-}CH_3$)
(2) 1′,1‴-Bis(*m*-methylbenzyl)biferrocenium triiodide ($X{=}m\text{-}CH_3$)
(3) 1′,1‴-Bis(*p*-methylbenzyl)biferrocenium triiodide ($X{=}p\text{-}CH_3$)

The introduction of a methyl group to the benzyl substituent in 1′,1‴-dibenzylbiferrocene is expected to influence the packing of those cations in the solids. In the present paper, the triiodide salts of 1′,1‴-bis(*o*-methylbenzyl)-, 1′,1‴-bis(*m*-methylbenzyl)-, and 1′,1‴-bis(*p*-methylbenzyl)biferrocene (Fig. 1) were synthesized and investigated by means of Mössbauer spectroscopy in order to study the effects of the substituents on the valence states of iron atoms.

Experimental

Materials. 1′,1‴-Bis(*o*-, *m*-, and *p*-methylbenzyl)biferrocene were prepared by Ullmann coupling at 100—110 °C for 18 h of 1-bromo-1′-(*o*-, *m*-, and *p*-methylbenzyl)ferrocene, respectively. The products were checked by using ^{1}H NMR and elemental analysis. The data of elemental analysis for 1′,1‴-bis(*o*-, *m*-, and *p*-methylbenzyl)biferrocene are shown below, respectively: Found: C, 74.51; H, 4.64%, Found: C, 73.24; H, 6.57%, and Found: C, 75.18; H, 6.74%. Calcd for $C_{36}H_{34}Fe_2$: C, 74.76; H, 5.93%

The triiodide salts were prepared by partial oxidation of the corresponding 1′,1‴-bis(*o*-, *m*-, and *p*-methylbenzyl)-biferrocene in benzene with a stoichiometric amount of I_2. All the analytical data of 1′,1‴-bis(*o*-, *m*-, and *p*-methylbenzyl)biferrocenium triiodide salt are shown below, respectively: Found: C, 45.01; H, 4.17%, Found: C, 44.61; H, 4.19%, and Found: C, 42.99; H, 3.98%. Calcd for $C_{36}H_{34}Fe_2I_3$: C, 45.08; H, 3.57%.

Mössbauer Spectroscopic Measurements. ^{57}Co(Rh) moving in a constant-acceleration mode was used as the radioactive source for Mössbauer spectroscopic measurements. Mössbauer spectra were obtained by using an Austin Science Associates Mössbauer spectrometer and a proportional counter. The isomer shifts were referred to a metallic iron foil. The Mössbauer parameters were obtained by least-squares fitting to Lorentzian peaks.

Results and Discussion

Mössbauer spectroscopic measurements of 1′,1‴-bis(methylbenzyl)biferrocenes were carried out at 78 and 298 K. The Mössbauer spectroscopic data are shown in Table 1 together with those of 1′,1‴-dibenzylbiferrocene. It can be seen from Table 1 that all the spectral data show ferrocene-type bivalent iron, although the value of quadrupole splitting (ΔE_q) for 1′,1‴-bis(*o*-methylbenzyl)biferrocene is a little smaller than those of 1′,1‴-bis(*m*-methylbenzyl)- and 1′,1‴-bis(*p*-methylbenzyl)biferrocene.

Mössbauer spectroscopic measurements of 1′,1‴-bis(methylbenzyl)biferrocenium triiodides were carried out at 78 and 298 K. The Mössbauer spectra of 1′,1‴-bis(*o*-methylbenzyl)-, 1′,1‴-bis(*m*-methylbenzyl)-, and 1′,1‴-bis(*p*-methylbenzyl)biferrocenium triiodide are shown in Figs. 2, 3, and 4, respectively. These Mössbauer spectroscopic data are summarized in Table 2 together with those of 1′,1‴-dibenzylbiferrocenium triiodide.

Table 1. Mössbauer Parameters

Compound	Temperature /K	$\delta^{a)}$/mm s^{-1}	ΔE_q/mm s^{-1}
1′,1‴-Dibenzyl-biferrocene	298	0.45	2.31
	78	0.53	2.32
1′,1‴-Bis(*o*-methyl benzyl)biferrocene	298	0.44	2.28
	78	0.52	2.29
1′,1‴-Bis(*m*-methyl-benzyl)biferrocene	298	0.45	2.31
	78	0.53	2.32
1′,1‴-Bis(*p*-methyl-benzyl)biferrocene	298	0.44	2.30
	78	0.53	2.32

a) Isomer-shift data are reported with respect to metallic iron foil.

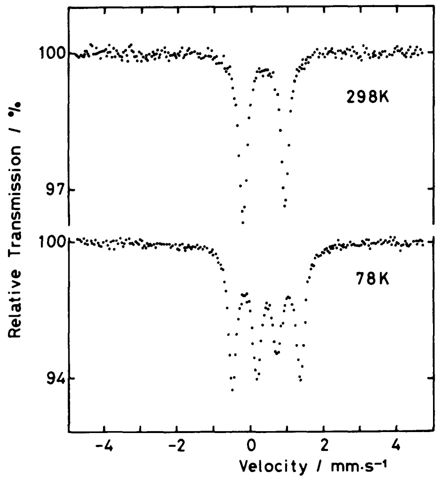

Fig. 2. Mössbauer spectra of 1′,1‴-bis (*o*-methylbenzyl) biferrocenium triiodide at 78 and 298K.

1′,1‴-Dibenzylbiferrocenium triiodide shows the remarkable temperature-dependence in its Mössbauer spectra; i.e., the spectra are of the trapped-valence type at low temperatures and of the averaged-valence type at high temperatures near room temperature.

Mixed-valence states observed in the present study depend on the position of methyl group in the benzyl

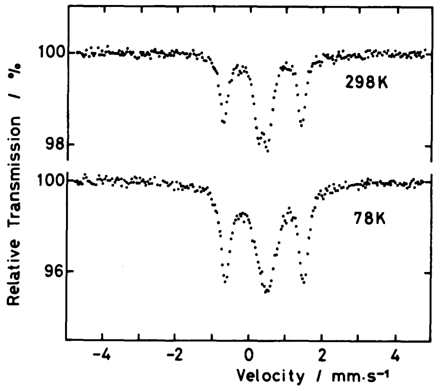

Fig. 3. Mössbauer spectra of 1′,1‴-bis (*m*-methylbenzyl) biferrocenium triiodide at 78 and 298K.

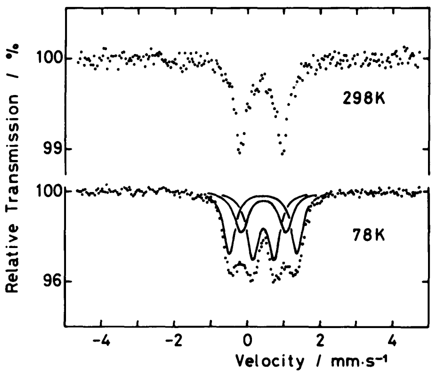

Fig. 4. Mössbauer spectra of 1′,1‴-bis(*p*-methylbenzyl) biferrocenium triiodide at 78 and 298K.

Table 2. Mössbauer Parameters

Compound	Temperature/K	$\delta^{a)}$/mm s^{-1}	ΔE_q/mm s^{-1}	Area/%
1′,1‴-Dibenzylbiferrocenium$^+$ I_3^-	298	0.44	1.11	100
	78	0.53	2.00	43
		0.51	1.21	14
		0.53	0.44	43
1′,1‴-Bis(*o*-methylbenzyl)-biferrocenium$^+$ I_3^-	298	0.44	1.14	100
	78	0.53	1.85	50
		0.54	0.57	50
1′,1‴-Bis(*m*-methylbenzyl)-biferrocenium$^+$ I_3^-	298	0.44	2.14	45
		0.45	0.26	55
	78	0.53	2.15	42
		0.58	ca. 0	58
1′,1‴-Bis(*p*-methylbenzyl)-biferrocenium$^+$ I_3^-	298	0.46	1.13	100
	78	0.53	1.87	35
		0.54	1.24	28
		0.54	0.59	37

a) Isomer-shift data are reported with respect to metallic iron foil.

substituent. In 1′,1‴-bis(*o*-methylbenzyl)biferrocenium triiodide, the spectrum at 78 K consists of an inner and an outer doublet with nearly 1 : 1 ratio in areal intensity, which are ascribable to ferricenium-like tervalent and ferrocene-like bivalent iron, respectively, while the spectrum consists of only one doublet at room temperature. The Mössbauer spectroscopic data for the doublet at 298 K show a close resemblance to those for 1′,1‴-dibenzylbiferrocenium triiodide at 298 K.

On the other hand, the Mössbauer spectra obtained in 1′,1‴-bis(*m*-methylbenzyl)biferrocenium triiodide show a trapped-valence state both at 78 and 298 K. Although the Mössbauer spectrum of 1′,1‴-bis(*p*-methylbenzyl)biferrocenium triiodide at 298 K shows an averaged-valence state as in the case of 1′,1‴-bis(*o*-methylbenzyl)biferrocenium triiodide at 298 K, the spectrum at 78 K seems to have both a trapped-valence state and an averaged-valence state.

The values of ΔE_q of outer ferrocene-like doublet found in *o*- and *p*-methylbenzyl derivatives at 78 K are a little smaller than that found in *m*-methylbenzyl derivative at 78 K, while the values of ΔE_q of inner ferricenium-like doublet found in *o*- and *p*-methylbenzyl derivatives at 78 K are a little larger than that found in *m*-methylbenzyl derivative at 78 K. This suggests that the interaction between Fe(II) and Fe(III) in *o*- and *p*-methylbenzyl derivatives is stronger than that in *m*-methylbenzyl derivative even at 78 K.

These results suggest that the position of methyl group in the benzyl substituent has important effects on the mixed-valence states of 1′,1‴-bis(methylbenzyl)-biferrocenium triiodides. In 1′,1‴-bis(*m*-methylbenzyl)biferrocenium triiodide, one of the terminal iodine atoms of the I_3^- anion is supposed to be situated closer to the Fe(III) atom of a cation(both at 78 and at 298 K) based on the assumption made on the studies of 1′,1‴-di-*n*-butyl- and 1′,1‴-dibenzylbiferrocenium triiodide[4] and the ^{129}I-Mössbauer spectroscopic studies of ferricenium, biferrocenium and 1′,1‴-dihalobiferrocenium iodide salts,[5] although further structual information on the compounds used is needed to verify the assumption.

References

1) "Mixed-Valence Compounds," ed by D. B. Brown, D. Reidel Publishing Company, Dordrecht (1980).

2) W. H. Morrison, Jr. and D. N. Hendrickson, *J. Chem. Phys.*, **59**, 380 (1973).

3) S. Iijima, R. Saida, I. Motoyama, and H. Sano, *Bull. Chem. Soc. Jpn.*, **54**, 1375 (1981).

4) T.-Y. Dong, D. N. Hendrickson, K. Iwai, M. J. Cohn, S. J. Geib, A. L. Rheingold, H. Sano, I. Motoyama, and S. Nakashima, *J. Am. Chem. Soc.*, **107**, 7996 (1985).

5) M. Katada, S. Nakashima, Y. Uchida, I. Motoyama, H. Sano, H. Sakai, and Y. Maeda, *J. Radioanal. Nucl. Chem., Lett.*, in press.